



US009409867B2

(12) **United States Patent**
Rigo et al.

(10) **Patent No.:** **US 9,409,867 B2**
(45) **Date of Patent:** ***Aug. 9, 2016**

(54) **LIGANDS OF THE BENZO[H]QUINOLINE CLASS AND TRANSITION METAL COMPLEXES CONTAINING THEM AND USE OF SAID COMPLEXES AS CATALYSTS**

6,878,852 B2 4/2005 Rautenstrauch et al.
7,638,628 B2 12/2009 Baratta et al.
8,614,322 B2 * 12/2013 Rigo C07D 221/10
546/10

(71) Applicant: **UNIVERSITA' DEGLI STUDI DI UDINE**, Udine (IT)

FOREIGN PATENT DOCUMENTS

JP H06-047235 7/1991
WO WO2005/105819 11/2005

(72) Inventors: **Pierluigi Rigo**, Udine (IT); **Walter Baratta**, Udine (IT); **Katia Siega**, Tarvisio (IT); **Giorgio Adolfo Chelucci**, Sassari (IT); **Maurizio Ballico**, Udine (IT); **Santo Magnolia**, Udine (IT)

OTHER PUBLICATIONS

(73) Assignee: **Universita' Degli Studi Di Udine**, Udine (IT)

Johnstone, R.A. et al. Heterogeneous Catalytic Transfer Hydrogenation and Its Relation to Other Methods for Reduction of Organic Compounds. Chem. Rev. 1985, vol. 85, p. 141.*
Dorwold, FZ. Side Reactions in Organic Synthesis. Wiley. 2005, preface.*

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

This patent is subject to a terminal disclaimer.

A. C. Hillier, H. M. Lee, E. D. Stevens, S. P. Nolan, Organometallics 2001, 20, pp. 4246-4252.

(21) Appl. No.: **14/083,710**

Baratta, W. et al. Ruthenium(II) Terdentate CNN Complexes: Superlative Catalysts for the Hydrogen-Transfer Reduction of Ketones by Reversible Insertion of a Carbonyl Group into the Ru-H Bond. Angew. Chem. Int. Ed. . . . 2005, vol. 44, p. 6214.

(22) Filed: **Nov. 19, 2013**

Baratta, W. et al., "New Benzo(h)quinoline-Based Ligands and their Pincer Ru and Os Complexes for Efficient Catalytic Transfer Hydrogenation of Carbonyl Compounds," Chemistry (Weinheim an Der Bergstrasse, Germany), vol. 14, No. 30, Sep. 2008, pp. 9148-9160, XP-002510333. (ISR).

(65) **Prior Publication Data**

US 2014/0179923 A1 Jun. 26, 2014

Baratta, W. et al., "Ruthenium(III) Terdentate CNN Complexes: Superlative Catalysts for the Hydrogen-Transfer Reduction of Ketones by Reversible Insertion of a Carbonyl Group into the Ru-H Bond," Angewandte Chemie (International Ed. in English) Sep. 2005, vol. 44, No. 38, pp. 6214-6219, XP-002510286. (ISR) (Written Opinion) (IPRP)

Related U.S. Application Data

(62) Division of application No. 12/452,553, filed as application No. PCT/EP2008/059060 on Jul. 11, 2008, now Pat. No. 8,614,322.

C. Thaumazet, M. Melaimi, L. Ricard, F. Mathey, P. Le Floch, Organometallics 2003, 22, pp. 1580-1581.

(30) **Foreign Application Priority Data**

Jul. 11, 2007 (IT) PD2007A0237

C. W. Jung, P. E. Garrou, P. R. Hoffman, K. G. Caulton, Inorg. Chem. 1984, 23, pp. 726-729.

(51) **Int. Cl.**

C07D 221/06 (2006.01)
C07D 221/10 (2006.01)
C07F 15/00 (2006.01)
C07C 1/22 (2006.01)
C07C 29/14 (2006.01)
C07C 29/143 (2006.01)

Cabeza et al. Triruthenium and Triosmium Carbonyl Cluster Complexes Containing Bridging Ligands Derived from 2-amino-7,8-benzoquinoline. Organometallics. 2002, vol. 21, p. 5055.

Cappelli et al., J. Med. Chem. 1998, 41, pp. 728-741.

(Continued)

(52) **U.S. Cl.**

CPC **C07D 221/10** (2013.01); **C07C 1/22** (2013.01); **C07C 29/14** (2013.01); **C07C 29/143** (2013.01); **C07F 15/0026** (2013.01); **C07F 15/0053** (2013.01)

Primary Examiner — Rita Desai

Assistant Examiner — Ben S Michelson

(58) **Field of Classification Search**

None
See application file for complete search history.

(74) Attorney, Agent, or Firm — Reed Smith LLP; Lisa A. Chiarini

(56) **References Cited**

U.S. PATENT DOCUMENTS

6,184,381 B1 2/2001 Ikariya et al.
6,372,931 B1 4/2002 Blacker et al.
6,451,727 B2 9/2002 Zhang
6,545,188 B2 4/2003 Blacker et al.

(57) **ABSTRACT**

A new class of ligands derived from benzo[h]quinoline are described and these ligands are used to prepare several novel transition metal complexes. The complexes are preferably of the group VIII transition metals iron, ruthenium or osmium, with the benzo[h]quinoline ligands acting as tridentate ligands. The complexes described are proved to be very active catalysts for the reduction of ketones and aldehydes to alcohols, via hydrogen transfer and hydrogenation reactions. These compounds hence can be usefully employed as catalysts in said reduction reactions.

7 Claims, No Drawings